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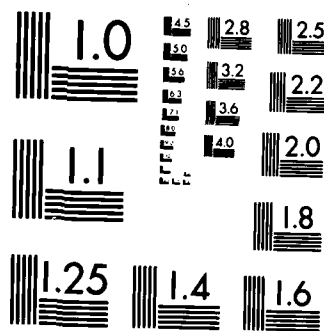
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Task No. NR 051-579

TECHNICAL REPORT NO. 3

"PROSPECTS FOR A NEW KIND OF SYNTHESIS: ASSEMBLY  
OF MOLECULAR COMPONENTS TO ACHIEVE FUNCTIONS"

by

Mark S. Wrighton

Prepared for Publication

in the

Comments on Inorganic Chemistry

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May 16, 1985

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR TR3	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Prospects for a New Kind of Synthesis: Assembly of Molecular Components to Achieve Functions"		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Mark S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0553
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Rm. 6-335 Massachusetts Institute of Technology Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-579
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia		12. REPORT DATE May 16, 1985
		13. NUMBER OF PAGES 34
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; reproduction is permitted for any purpose of the United States Government; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared for publication in <u>Comments on Inorganic Chemistry</u>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Molecular components, aggregate chemical systems, electronic devices, Sensors		
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(20) aspects of systems synthesis. These example systems include multi-component catalysts, the photosynthetic apparatus for solar energy conversion, diodes and transistors. Originator Supplied Keywords include:

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[Prepared for Publication in Comments on Inorganic Chemistry]

Prospects for a New Kind of Synthesis: Assembly  
of Molecular Components to Achieve Functions

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Abstract

Molecular scientists now have an opportunity to add an important new dimension to synthesis. Preparation of chemical systems, comprising two or more components, to achieve a function is possible. While rational strategies exist for some simple systems, major advances in fundamental reaction chemistry at the molecular and macromolecular level, especially at interfaces are required to achieve practically significant synthetic objectives. Synthetic chemical systems inspired by nature and microelectronic devices illustrate some of the aspects of systems synthesis. These example systems include multi-component catalysts, the photosynthetic apparatus for solar energy conversion, diodes, and transistors.

## Introduction

The aim of this article is to raise the consciousness of inorganic chemists to the opportunities associated with the application of molecular science to the preparation of "systems" having functions derived from judicious assembly of molecular components. It can be argued that molecular synthesis has progressed to a point such that molecules of any complexity can be prepared, provided sufficient resources are applied to the problem. The preparation of vitamin B<sub>12</sub>,<sup>1</sup> among other examples, stands as one of the crowning achievements of molecular synthesis. While the synthesis of vitamin B<sub>12</sub> cannot be regarded as "practical", the synthesis of vitamin B<sub>12</sub> and numerous other large, structurally complex, natural substances illustrates that the perceptive application of synthetic methodology and the continuing development of new, useful synthetic methods allows the conclusion that most any desired molecule can be prepared. With this assumption, it is thus evident that there exists an opportunity to begin assembling "systems" from synthetic, molecular components.

A large group of inorganic chemists have focused their attention on molecules. Structural characterization of "small" molecules has comprised a major accomplishment in inorganic chemistry, beginning with Werner's classic work on six-coordinate complexes<sup>2</sup> and including pioneering work on metal carbonyls by Hieber,<sup>3</sup> sandwich and other organometallic complexes by Fischer<sup>4</sup> and Wilkinson,<sup>5</sup> metal-metal bonded complexes by Cotton,<sup>6</sup> and models of metal-containing biological molecules by Holm.<sup>7</sup> As for other molecules, the structural characterization of molecules containing metals has led to considerable understanding of reactions, and in many cases rational synthetic methodology has emerged for the preparation of molecules of great structural, chemical, and physical diversity. Elegant molecular

synthesis of metal containing substances has led to the preparation of new classes of materials, practically important catalysts, and molecules that elaborated understanding of electronic structure, bonding, reaction mechanisms, and the function of small molecules in large "systems", especially biological systems.

With the considerable knowledge presently available concerning the synthesis, structure, and reactions of inorganic molecules coupled with the fact that properly assembled molecules, as in natural biological systems, can achieve a function characteristic of the assembly, there exists an opportunity to undertake a new kind of chemical synthesis. The rational preparation of multi-component chemical "systems" of significant geometrical dimension, up to a few microns, is possible. It is now appropriate to define "system". A chemical system will be taken to be an assembly of at least two components that together yield a function characteristic of assembly. Examples of such systems can be found in nature and in man-contrived electronics. Discrete microelectronic devices provide realistic examples, because their size is sufficiently small (crucial dimensions of one micron, or less) that there is a realistic possibility that their discrete functions can be duplicated using assemblies of molecules. Illustrations of the synthesis of chemical systems, and conjecture concerning new ones, are developed below within the framework of duplicating functions of chemical systems found in nature or of discrete microelectronic devices.

#### Chemical Systems Inspired by Nature

There are many sub-systems of a living system that can serve as targets for chemical synthesis. The objective of the synthesis is not necessarily to duplicate exactly the natural system, but could be to synthesize a system that will duplicate the function of the natural system with components that might be abiological. Perhaps the smallest departure from a major theme of modern

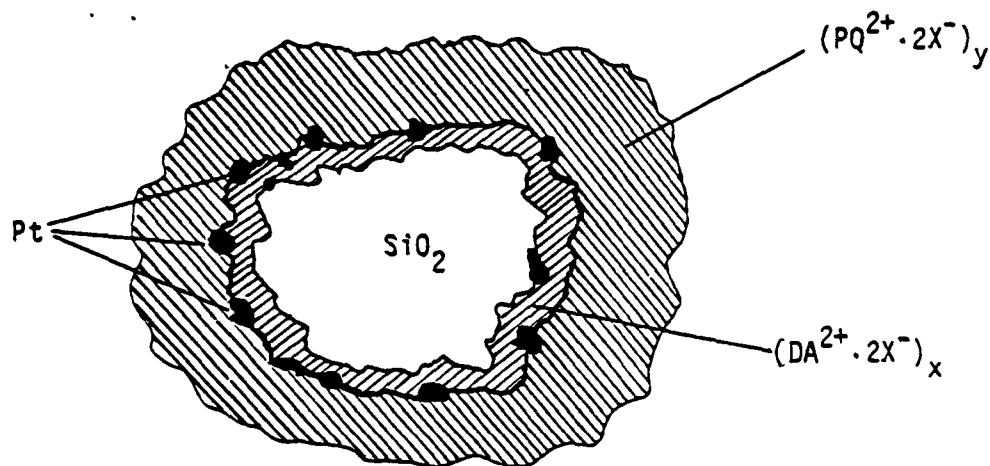


inorganic chemistry research is the synthesis of multi-component catalysts. Indeed, in this area systems synthesis would appear to be most straightforwardly understood. Accordingly, this area will be used as one concrete example where accomplishment is readily possible. A second example of an important subsystem in biology is the solar energy conversion apparatus that consists of many molecular components assembled in such a way that photoexcitation of an absorber molecule results in unidirectional electron transfer and, ultimately, the formation of thermodynamically unstable redox products. There are numerous other sub-systems of living systems aside from complicated catalysts and solar energy conversion, but these provide ample illustrative value. Successful chemical synthesis of such systems would likely lead to practical return as well as deeper understanding of biological-chemical systems.

Multi-Component Catalytic Systems. Molecular scientists have been very successful in synthesizing useful transition metal complex catalysts that operate under mild conditions to give good product specificity, high yields, and large rates. Excellent illustrations include the Sharpless asymmetric epoxidation catalyst,<sup>8</sup> Bosnich's asymmetric hydrogenation catalysts,<sup>9</sup> Schrock's alkyne metathesis catalysts,<sup>10</sup> and Collman's catalyst for the  $4e^-$  reduction of  $O_2$  to  $H_2O$ .<sup>11</sup> As important as such catalysts are, and as important as future efforts will continue to be, these are not examples of chemical systems, since the function is achieved with a single component. Single component function is, of course, crucial to the overall function of a system, but conventional molecular catalysis does not, generally, comprise a chemical system according to the definition above which requires that a system be an assembly of at least two components.

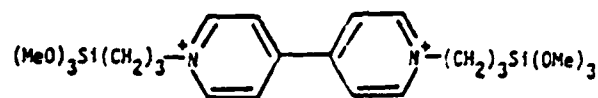
Nature provides many examples of multi-component catalysts. For example, biological systems appear to routinely catalyze complex, multi-electron redox reagents such as  $O_2$  (and a substrate) to product via multi-component systems. In such cases there often appears to be a site of "activation" or "binding" of the complex redox reagent coupled in some fashion to an apparatus for transferring electrons stepwise to the site. The function of such multi-component systems might be said to be the interconversion of complex, multi-electron, (typically inner-sphere) redox reagents and simple, one-electron, (typically outer-sphere) redox reagents.

As a modest example of a multi-component catalyst system consider the system represented by Scheme I.<sup>12</sup> The catalyst,  $[SiO_2](DA^{2+} \cdot 2X^- \cdot Pt)_x / (PQ^{2+} \cdot 2X^-)_y$ .



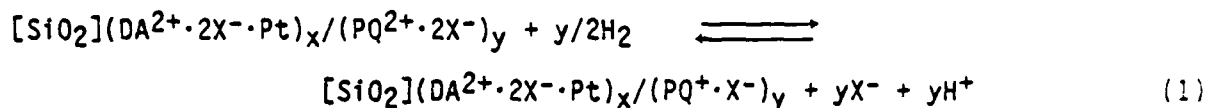
Scheme I. A multi-component catalyst system for the one-electron reduction of biological redox agents using  $H_2$  activation that then results in reduction of the  $(PQ^{2+})_n$  polymer coating the "buried" Pt particles. The  $(PQ^+)_n$  is capable of reducing large biological redox reagents ordinarily unaffected by  $H_2$  or by Pt surfaces exposed to  $H_2$ .<sup>12</sup>

has the function that it will interconvert the two-electron reductant  $H_2$ , in aqueous solution, and a one-electron, outer-sphere reductant of equivalent reducing power. The useful catalysis that can be achieved is the one-electron reduction of large biological redox reagents, such as horseradish peroxidase, that are generally difficult to reduce at interfaces and are inert to  $H_2$ . Notice that the system in Scheme I is structured in such a way that the site for  $H_2$  activation, the Pt, is buried under the  $(PQ^{2+} \cdot 2X^-)_y$  polymer derived from I.



I

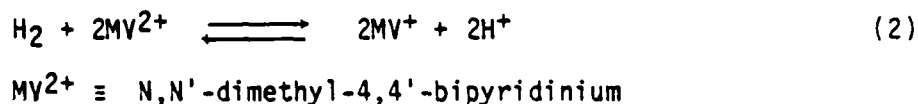
The small  $H_2$  molecule can diffuse through the outer coating of  $(PQ^{2+} \cdot 2X^-)_y$  to the Pt. The  $(PQ^{2+} \cdot 2X^-)_y$  polymer is in contact with the Pt particles which activate in aqueous solution. Thus, reduction of  $(PQ^{2+} \cdot 2X^-)_y$  polymer occurs reversibly according to equation (1). Large biological molecules cannot penetrate to the



site of  $H_2$  activation and are thus protected from hydrogenation and hydrogenolysis that might pose complications if the biological reagent were to contact the Pt.

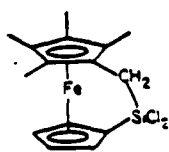
The function of the two-component system represented in Scheme I is to interconvert  $H_2$  and one-electron reductants. In nature this function appears to be achievable with the enzyme hydrogenase<sup>13</sup> which inspired the synthesis of

catalyst in Scheme I. Hydrogenase will catalyze the process represented by equation (2), and can be regarded as a single component catalyst. The



two-component catalyst of Scheme I does what the single-component enzyme does, but the synthetic system of Scheme I operates by a different mechanism.

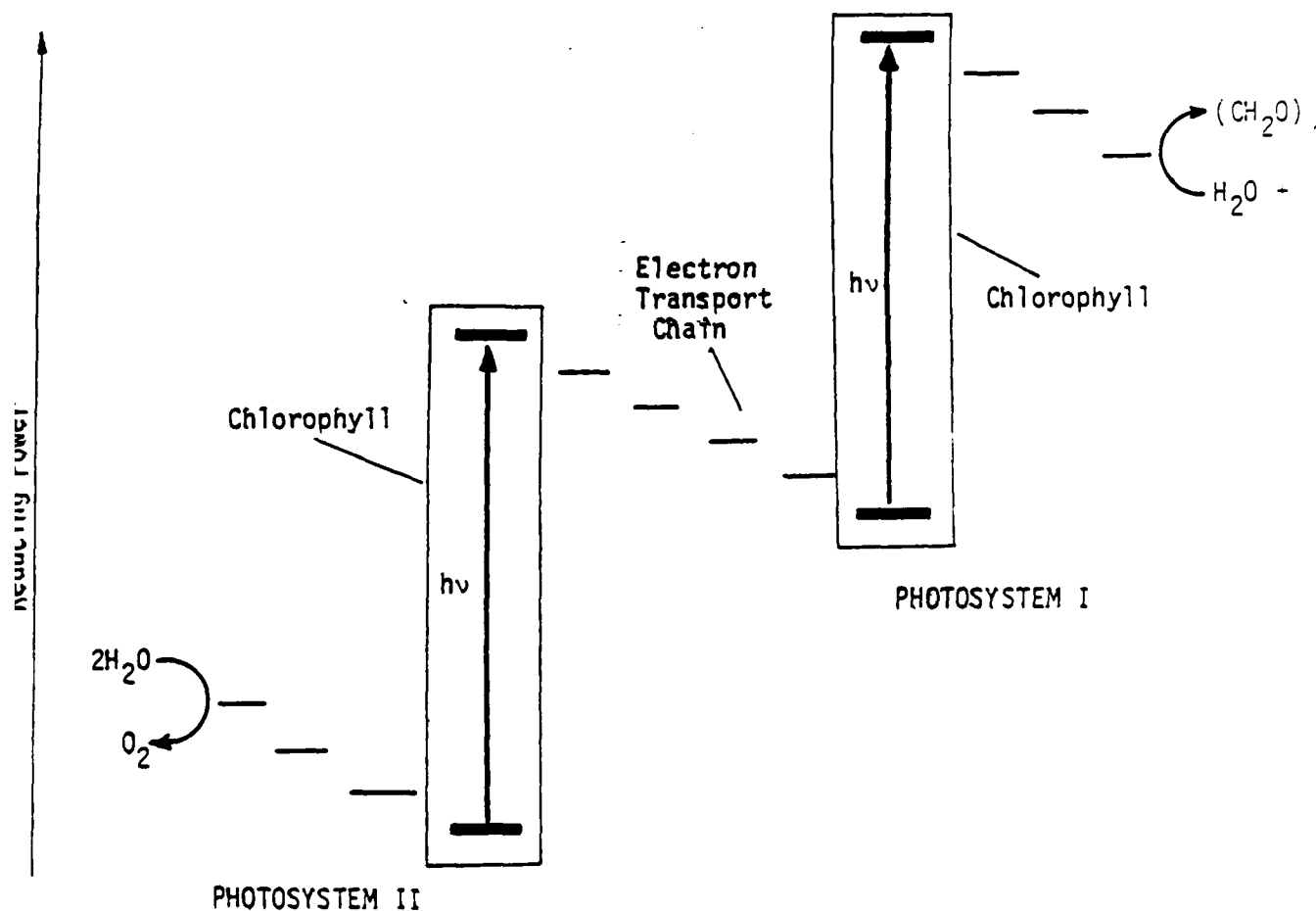
The two-component system in Scheme I can be extended to a three-component system by anchoring a redox enzyme to the outermost portion of the  $(\text{PQ}^{2+} \cdot 2\text{X}^-)_y$  polymer. It is known that many redox enzymes can be rapidly equilibrated with the  $\text{MV}^{2+}/^+$  solution mediator system.<sup>14</sup> It therefore appears logical to extrapolate the system in Scheme I to a three-component catalyst with the function of effecting catalytic reduction with  $\text{H}_2$ . Such a system has credibility, because it is known that immobilization of enzymes onto polymers is possible, and can lead to better enzyme durability.<sup>15</sup> Judicious assembly of noble metals, redox polymers, and enzymes makes possible many complicated catalytic processes. The idea can be easily extended to include oxidation with  $\text{O}_2$ . For example,  $\text{SiO}_2$  microspheres could be modified with  $\text{Ru}/\text{RuO}_2$  followed by derivatization with a ferrocene-based polymer, such as one derived from hydrolysis of reagent II,<sup>16</sup> and capped with a redox enzyme such as glucose oxidase.



II

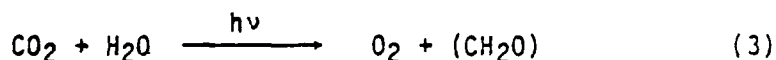
The function would be to oxidize glucose with  $O_2$ . The Ru/RuO<sub>2</sub> should activate  $O_2^{1-}$  which results in the oxidation of the ferrocene-based polymer which in turn equilibrates with the glucose oxidase<sup>18</sup> that oxidizes glucose. The point is that each of the three components serves an individual function which gives an aggregate function not achievable with any one component alone. These specific ideas should serve to illustrate what is meant by multi-component catalysts and that such catalyst systems can, in fact, be made by rational means using existing knowledge.

Photodiode-Systems: A Molecular Approach. Scheme II illustrates the familiar



Scheme II. Representation of the "Z-scheme" for photosynthesis showing two photosystems and an aggregate system to drive oxidation of  $H_2O$  and reduction of  $CO_2$ .

"Z-scheme" representing the essential features of the natural system for the conversion of optical energy to chemical energy in the form of redox products derived from CO<sub>2</sub> and H<sub>2</sub>O, equation (3).<sup>19</sup> The natural system is clearly one



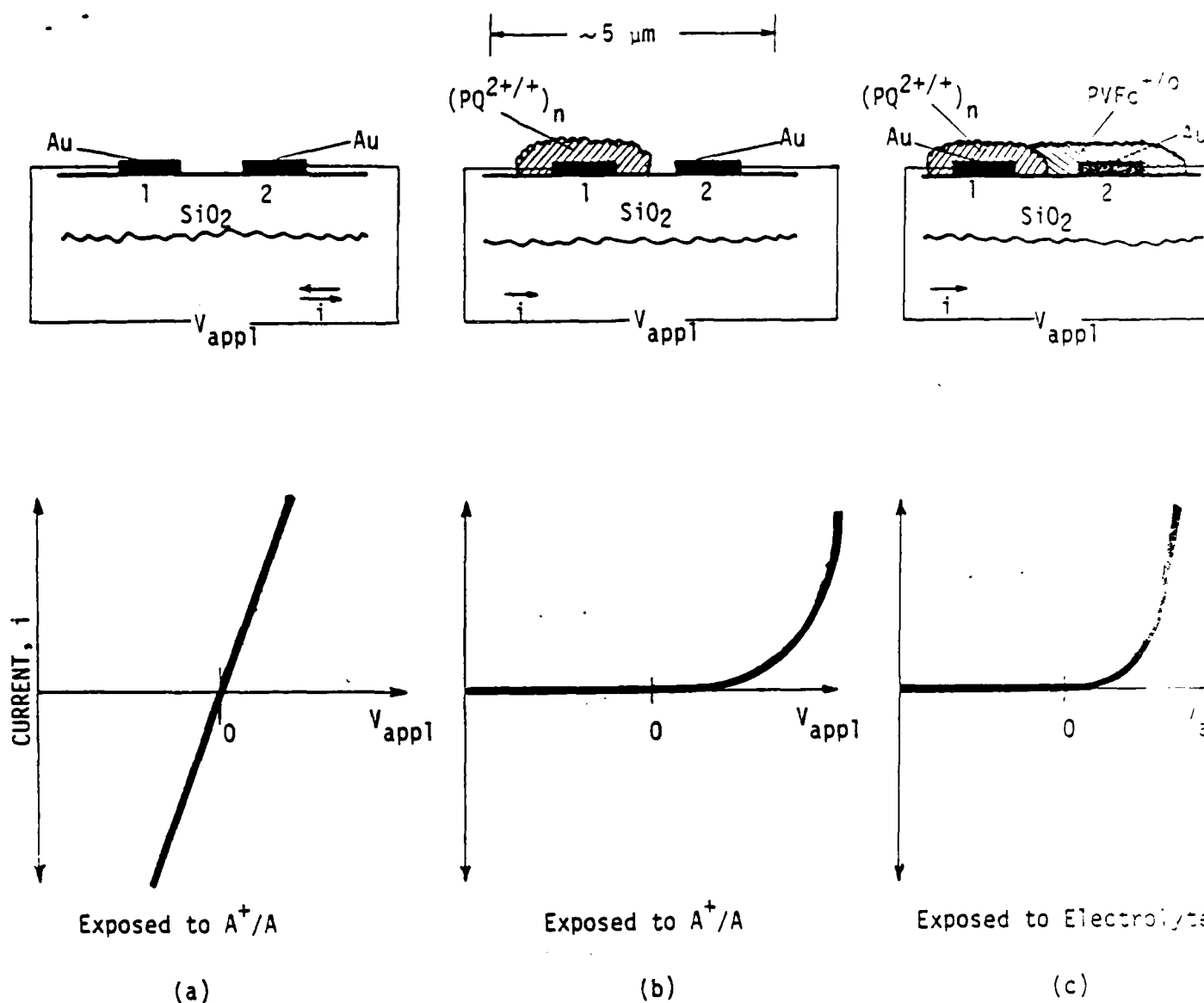
based on molecules, and thus provides an existence proof for molecule-based systems for solar energy conversion. In the area of research aimed at chemical approaches to solar energy conversion and storage there are many examples of efforts to devise chemical systems that mimic the function of the natural photosynthetic apparatus.

There are four important features of the photosynthetic apparatus. First there is a component for light absorption based on chlorophyll. Second, there is a structured arrangement of electron donor and acceptor reagents that function in such a way that excited state, one-electron reaction of the chlorophyll is irreversible. Electrons are transferred unidirectionally across significant distances to yield geometrically segregated oxidants and reductants. Third, there are catalysts that can apparently equilibrate with one-electron oxidants and reductants to effect the multi-electron oxidation of H<sub>2</sub>O and reduction of CO<sub>2</sub>. And fourth, the system involves two photosystems, presumably nature's way of effecting the formation of high energy redox products with good efficiency. It is well known that threshold response solar conversion systems can operate with higher efficiency when more than one light absorption system is used.<sup>20</sup>

The function of the photosynthetic system can be achieved with semiconductor based photoelectrochemical cells. Scheme III illustrates a double

approaches the formal potential of the  $(PQ^{2+}/^+)_n$  redox system,  $\sim -0.55V$  vs. SCE. Thus when a potential is applied to the two electrodes significant current passes only when the negative lead is attached to the  $(PQ^{2+}/^+)_n$ -modified electrode. Moreover, the potential required is of the order of  $\sim 0.9V$ , the difference in  $E^\circ$ 's of the  $(PQ^{2+}/^+)_n$  and the  $Fe(n^5-C_5H_5)^{+}/0$ . Significant current does not flow when the potential is applied in the opposite direction, because the reverse of the reaction represented by equation (8) is up-hill by  $\sim 0.9V$ .  $Fe(n^5-C_5H_5)_2^0$  can penetrate the  $(PQ^{2+})_n$  polymer and be oxidized at the electrode surface. The current from such penetration will represent a contribution to the leakage current, but to the extent that penetration can be prevented the cell has a diode-like current-voltage curve with a threshold voltage more or less given by the difference in  $E^\circ$ 's of the two molecule based components.

The final portion of Scheme VIII illustrates a microelectrochemical diode based on the principles developed in the preceding paragraph.<sup>39</sup> In this case both of the molecule-based materials are immobilized onto closely-spaced microelectrodes such that the two redox polymers "contact" each other. The  $(PQ^{2+}/^+)_n$  system is again derived from I and the  $PVFc^{+}/0$  is the polyvinylferrocene redox system. As in the case where the  $Fe(n^5-C_5H_5)_2^{+}/0$  system is in solution, current flow occurs upon application of potential in one direction; at the  $(PQ^{2+}/^+)_n/PVFc^{+}/0$  interface charge only passes in one direction, analogous to the redox reaction given by equation (8). Moreover, since both molecule-based systems are immobilized the only mechanism for charge transport from one microelectrode to the other is via electron transfer through the polymer connecting one electrode with another. The structural arrangement of the system is such that the two molecule-based materials contact each other but each is in turn only in contact with one microelectrode. The only mechanism for charge transport from one microelectrode to the other is via a path that is unidirectional owing to the large driving force for the process represented



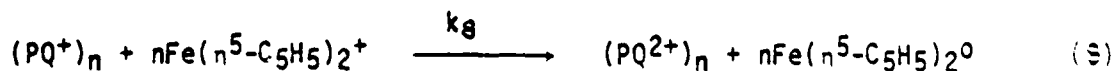
**Scheme VIII.** Two terminal microelectrochemical devices. (a) Both electrodes reversible to A<sup>+</sup>/A; (b) one redox polymer modified electrode only capable of only reducing A<sup>+</sup> to A; and (c) two redox polymer modified electrodes with a polymer/polymer contact such that current flows upon application of a potential sufficient to oxidize one polymer and reduce the other. In the current-voltage curves the voltage to the right of zero is for the positive lead connected to electrode 2.<sup>39</sup>



(molecule-based) materials in contact with one another. The analogy can be extended further by noting that the diode behavior of the ideal solid state devices depends in large measure on the difference in the work functions of the two materials. For electrochemical devices the diode current-voltage curves depend on the difference in the formal electrochemical potential of the two materials--- the equivalent of the difference in the work function of the two solid state materials of a conventional diode. Thus, molecule-based diodes are devices having properties that can be controlled by variation in the properties of the molecules that comprise them.

Scheme VIII illustrates several types of electrochemical devices presented within the framework of illustrating that rational synthesis of molecule-based diodes is possible. Consider first the situation represented by a cell having two equal area electrodes that are reversible to the redox couple  $A^+/A$  present in the solution such that  $[A] = [A^+]$ . Assuming that there are no electroactive materials other than  $A^+$  and  $A$ , application of a potential in either direction results in current flow such that  $A$  is oxidized to  $A^+$  at one electrode and  $A^+$  is reduced to  $A$  at the other, a symmetrical current-voltage curve about zero applied potential results.

To make the example in Scheme VIII more explicit, consider the redox couple to be  $Fe(n^5-C_5H_5)_2^{+/0}$ ,  $E^\circ = +0.45V$  vs. SCE,<sup>37</sup> in  $CH_3CN/0.1M [n-Bu_4N]ClO_4$ . If one of the electrodes is modified with polymer derived from I then that electrode is no longer reversible to the  $Fe(n^5-C_5H_5)_2^{+/0}$  redox couple.<sup>38</sup> Rather, only the reduction of  $Fe(n^5-C_5H_5)_2^+$  to  $Fe(n^5-C_5H_5)_2^0$  can be effected, equation (8). Moreover, the re-



duction can only be effected when the potential of the  $(PQ^{2+}/^+)_n$ -modified electrode

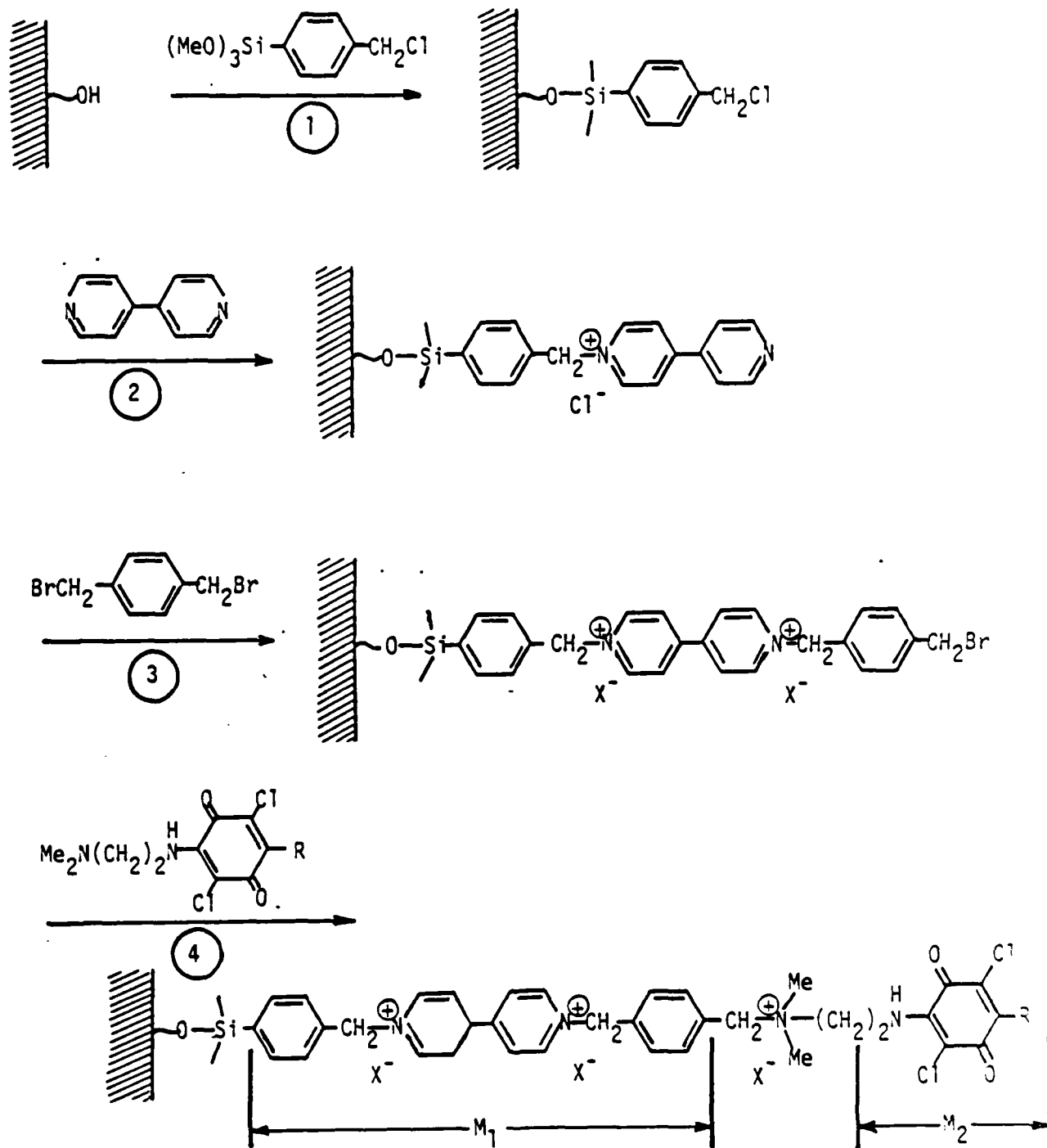
appears plausible. The small crucial dimensions of state-of-the-science microelectronics (sub-micron) can be spanned by macromolecules or organized molecular assemblies such as Langmuir-Blodgett multilayers. Thus, there is an opportunity to interface chemical (and biological) systems with solid state components prepared using more or less conventional microfabrication techniques. Employing microfabricated solid state components in synthetic, molecule-based chemical systems is analogous to using a natural enzyme as a component in a synthetic, molecule-based system inspired by natural systems. Two discrete microelectronic devices can be used to illustrate some of the issues here: diodes and transistors. Chemical systems, based on molecules as the crucial elements, can be fabricated which duplicate some of the properties of these devices. Molecule-based devices inspired by solid state microelectronics are not destined replace solid state devices on a near term timescale, rather the new devices may be useful for new applications where solid state devices may not be as useful. An especially promising practical application would be microsensors.

Devices Inspired By Diodes. Diodes are devices that allow current to pass upon the application of a potential in one direction but not when the applied potential is equal in magnitude but opposite in direction. Electrochemical devices, in general, can be configured in such a way that diode-like current-voltage curves can be obtained. However, recent work<sup>36</sup> on purposefully modified electrodes demonstrates clearly the ability to rationally prepare molecule-based diodes with crucial dimension (contact-to-contact) of less than 1  $\mu\text{m}$ . In solid state systems diode behavior can be obtained when two different materials are placed in electrical contact with one another, e.g. metal/semiconductor or p-/n-type semiconductor. Likewise, in electrochemical diodes, diode behavior can be brought about by placing two different

Molecule-based systems for light-induced charge separation do not function by the same mechanism as in semiconductor-based devices, but nonetheless the same net result can be achieved. In solid state devices photogenerated carriers are separated by the strong electric field associated with a p-n junction, semiconductor/metal interface, semiconductor/liquid electrolyte interface, or a photoconductor sandwiched between two conductors of different work function. The molecule-based systems achieve the function of useful charge separation via a series of thermodynamically down-hill redox events carrying reducing equivalents to a site geometrically distant from the site of oxidation in an ordered array of redox units. There are at least two concrete pathways by which such molecule-based systems can be synthesized, each with some precedent and each with advantages and disadvantages.

#### Chemical Systems Inspired by Microelectronics

By themselves the chemical components of microelectronic devices do not suggest that remarkable functions can be achieved. But clever organization of pedestrian semiconductors (Si, GaAs), metals (Au, Al), insulators (SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>) and dopants (B, P) makes possible the recent revolution in electrical engineering and computer science. Coupled with microfabrication techniques, the aggregate function that can be achieved from properties of electronic materials allows discrete devices such as diodes, transistors, lasers, and capacitors to be prepared in high density essentially in a two dimensional world, largely founded in elemental Si, except for optical devices. An appropriately organized array of discrete devices comprises an integrated circuit that allows larger functions to be realized than is possible with a discrete device which itself is typically prepared from several materials. It would appear possible to assemble chemical systems that achieve some of the functions of discrete solid state devices. Even "integration" of such systems

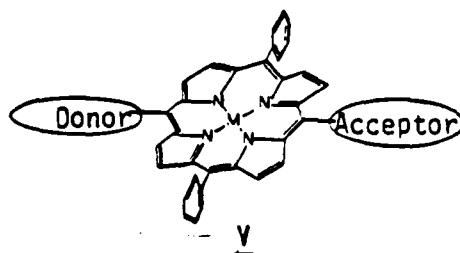


**Scheme VII.** Solid phase synthesis of a surface-confined macromolecule consisting of two redox units,  $\text{M}_1$  = a derivative of N,N'-dibenzyl-4,4'-bipyridinium and  $\text{M}_2$  = a derivative of 2,5-dichloro-p-benzoquinone.<sup>35</sup>

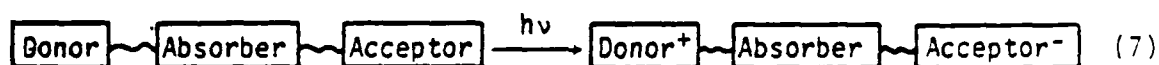
long-distance ( $\sim 20\text{\AA}$ ) excited state electron transfer to built-in acceptor molecules in a separate layer, and (3) that multilayers can be deposited on conductors and subsequently metallized to make a front and back contact.<sup>32</sup> In recent years some exciting possibilities have been raised concerning new applications of Langmuir-Blodgett techniques involving novel examples of monolayer film-forming molecules.<sup>32,33</sup>

A second synthetic methodology for systems like that in Scheme VI is inspired by the Nobel Prize winning work of Merrifield,<sup>34</sup> the "solid phase" synthesis of large macromolecules (non-polymeric, proteins) based on simple molecule building blocks, amino acids. The key to this synthetic methodology for the function of optical energy conversion is to use building blocks having functionality so that coupling can be carried out in a manner that yields an ordered arrangement of a light absorber and various electron donors and acceptors. Such solid phase synthesis can begin on electronic conductors to achieve the ultimate aim of efficient charge collection. The thrust of the idea is illustrated by the four step process in Scheme VII that has recently been demonstrated<sup>35</sup> as a prelude to a major effort to synthesize a complete system like that illustrated in Scheme VI. After the first step each successive step is the alkylation of a nitrogen. As in the Merrifield resin synthesis of a protein, the isolation of product occurs after each step by a physical separation of the solid. The result of the chemistry is a  $\text{SnO}_2$ -bound macromolecule consisting of two redox sub-units, a viologen derivative and a quinone. Note that the quinone bears a pendant  $-\text{NMe}_2$  group that can be alkylated in subsequent steps. It is apparent that a resin synthesis of macromolecules, consisting of well-defined redox sub-units; in an ordered array; and bound to a conductor, can be fruitful.

A start toward a system as envisioned in Scheme VI has been made by linking an electron acceptor and an electron donor to a porphyrin, V.<sup>29</sup> This follows



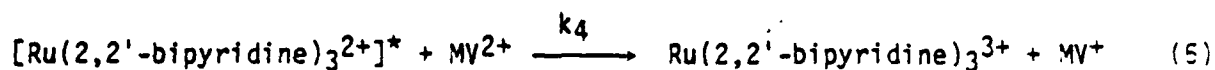
several reports of linked absorber and acceptor molecules that mimic the primary electron transfer systems in photosynthesis.<sup>30</sup> The three-component molecule macromolecule represented by V results in charge separation upon photoexcitation of the visible-light absorbing porphyrin unit as represented in equation (7). Such a



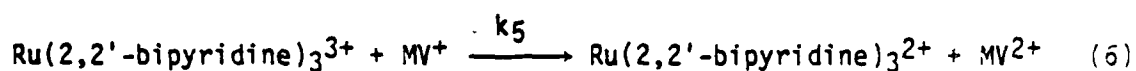
system illustrates the basic idea, but exploiting such charge separation is still precluded by rapid back electron transfer. What is needed to achieve useful energy conversion is greater geometrical separation between the oxidized donor and the reduced acceptor and a method for orienting an assembly of such molecule so that the charges can be collected by electronic conductors to generate electrical energy or by catalysts for irreversible fuel-forming reactions.

Prospects for synthesizing multi-molecule-based systems like that represented in Scheme VI seems possible by at least two methodologies, both of which can lead to a useful orientation on an electronic conductor. One synthetic methodology for synthesizing a system for useful light-induced, unidirectional electron transfer involves fabrication of multilayer films using the Langmuir-Blodgett technique.<sup>31</sup> Indeed, elegant work already demonstrates (1) fabrication of well-structured multilayers of significant (~500Å) dimension; (2) multilayers containing visible light absorbing molecules capable of

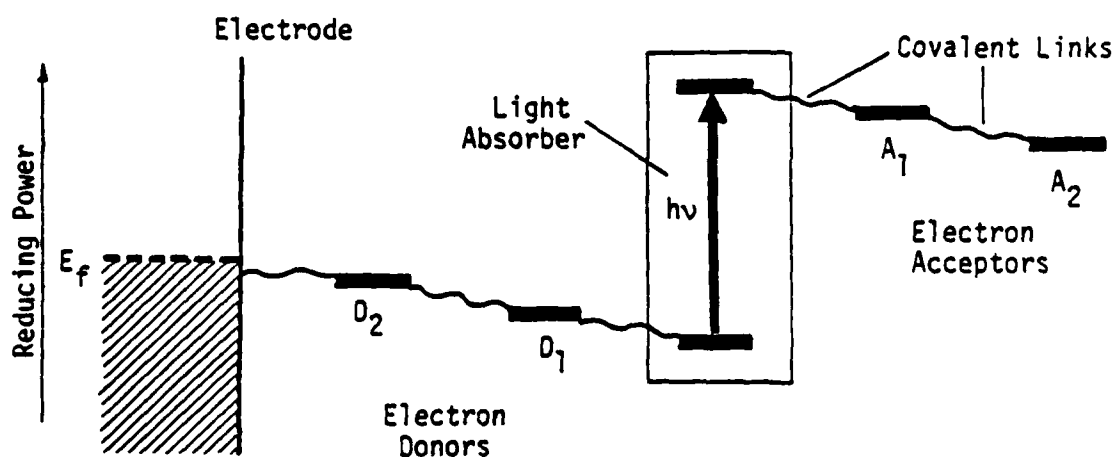
unidirectional, light-driven, (up-hill) electron transfer? Absorbing visible light with molecules that can transfer electrons to make high energy redox products is well known;<sup>27</sup> the excited state process represented by equation (5)



is but one example.<sup>28</sup> However, exploiting such high efficiency primary product formation is not possible, owing to rapid back electron transfer, equation (6),



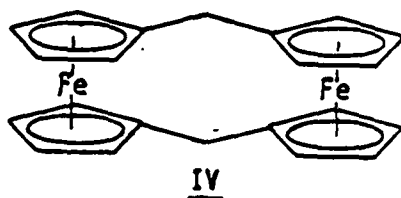
that degrades the excited state energy to heat. It should be possible to assemble macromolecular (non-polymeric) molecules, built from smaller molecules that have the function of absorbing light and transferring electrons in only one direction, Scheme VI. At least on paper, a molecule-based system can be devised that will duplicate a crucial part of the photosynthetic apparatus.



Scheme VI. Architecture of a molecular system for light absorption followed by unidirectional electron transfer.

redox polymers from I or III have redox potentials that are sufficiently negative that a good photovoltage is expected for many visible light-responsive photocathodes including p-type Si, WS<sub>2</sub>, InP, and a-Si:H.<sup>25</sup> Catalysis of the H<sub>2</sub> evolution reaction can be effected via equilibration of the Rh particles with the polymer; the Rh serves to equilibrate the redox polymer with the (H<sub>2</sub>O/H<sub>2</sub>) redox couple. The redox polymer/Rh system is used to convert one-electron-at-a-time photoexcitation events to efficient two-electron reduction of H<sub>2</sub>O. The entire assembly mimics one of the photosystems in photosynthesis.

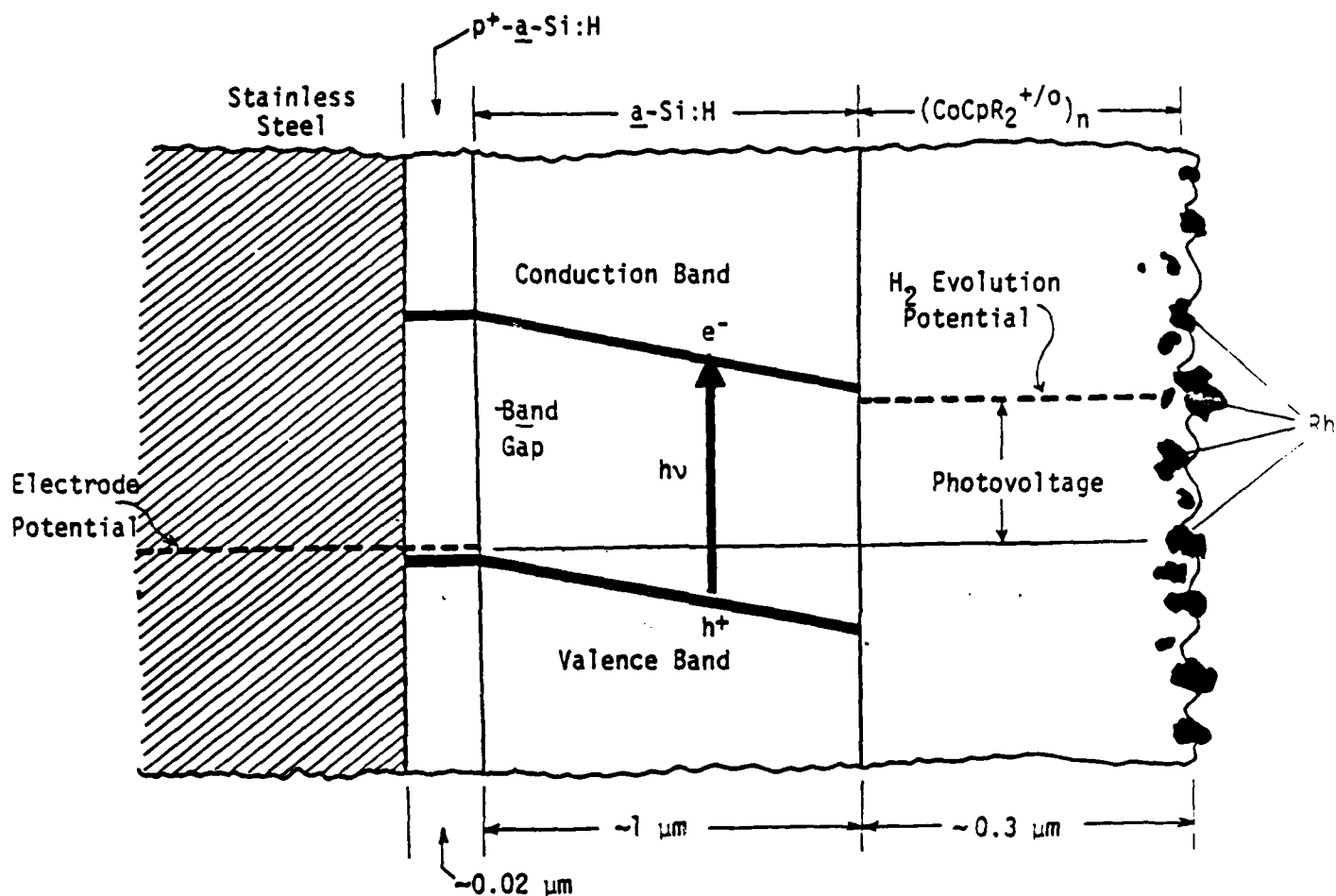
The particulate Rh catalyst for the H<sub>2</sub> evolution, in principle, could be replaced with a molecular catalyst. However, good catalyst molecules, other than the enzyme hydrogenase, for this purpose are not known. Species derived from IV



are H<sub>2</sub> evolution catalysts, but the turnover frequency is low and the system only works in very strong acid.<sup>26</sup> Replacing the Rh with a non-noble metal-containing catalyst would be important in lowering the cost of the catalyst. For the reasons outlined above in the section on multi-component catalysts the molecule-based redox polymer can represent a good way to interface the electrode with enzyme catalysts including hydrogenase. A p-type semiconductor/redox polymer/hydrogenase system could duplicate the function of one of the photosystems of photosynthesis with two of the components being molecule based, the electron relay system and the catalyst.

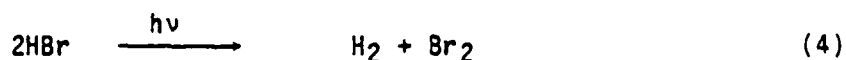
What are the prospects for molecule-based systems to achieve the function of





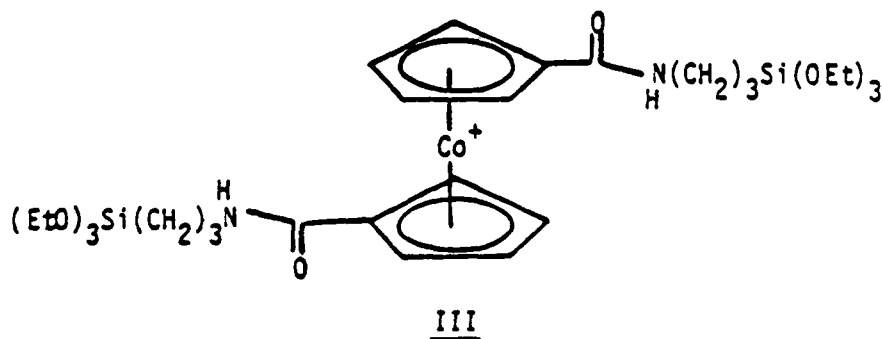
**Scheme V.** A thin film, catalytic photoelectrode for  $\text{H}_2$  evolution.<sup>25</sup> The  $a\text{-Si:H}$  intrinsic and  $p^+$ -doped, can be made by a deposition from  $\text{SiH}_4$ , and provides the mechanism for charge separation after photoexcitation. The  $(\text{CoCpR}_2^{+/0})_n/\text{Rh}$  is a catalyst system for rapidly accepting one-electron-at-a-time from the photoexcited  $i\text{-a-Si:H}$  and effecting  $\text{H}_2$  evolution via reduction of  $\text{H}_2\text{O}$ .

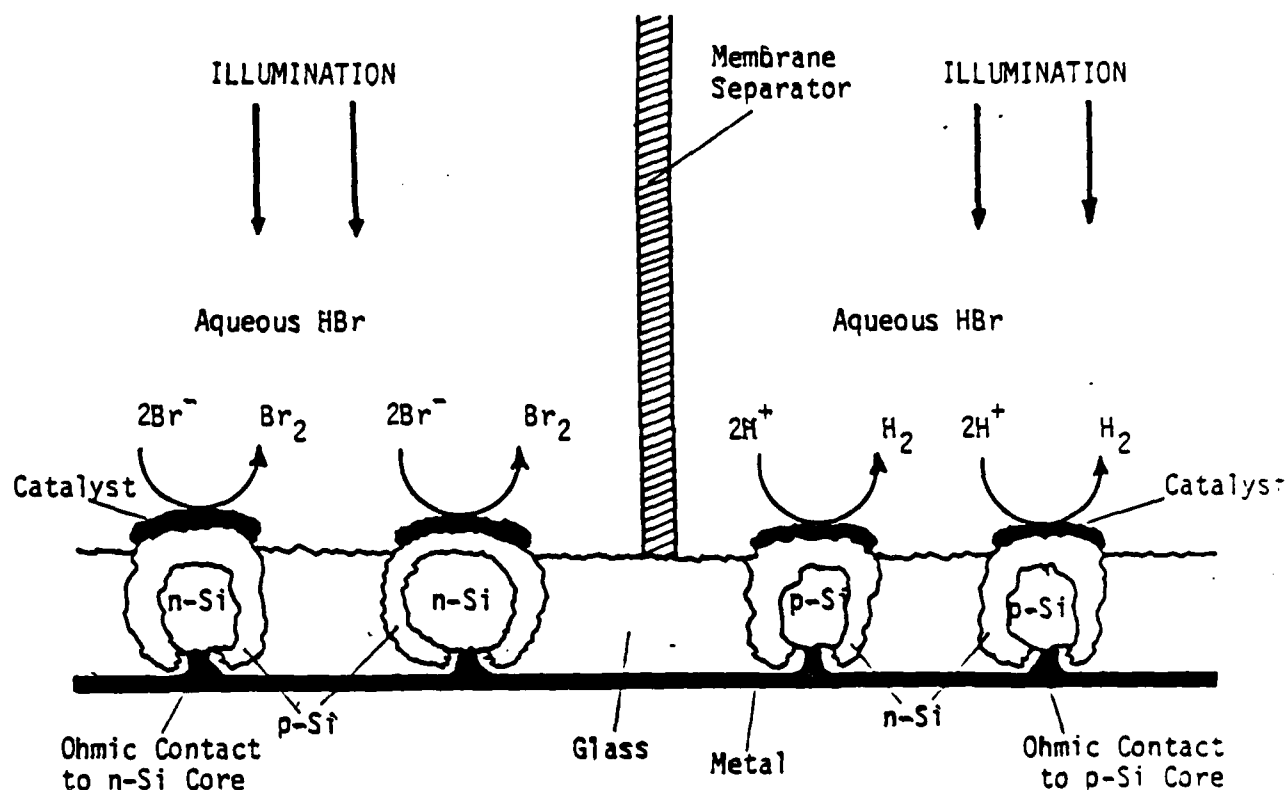
effect the process represented by equation (4).<sup>22</sup> This device with its various



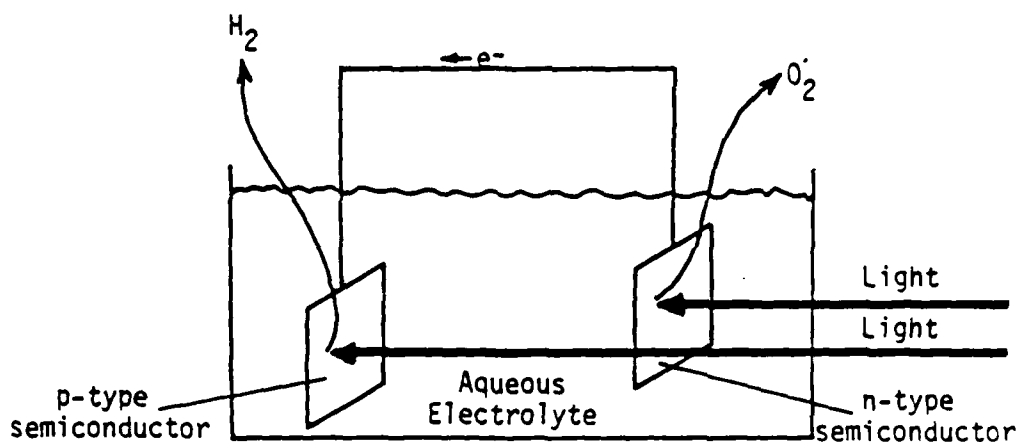
components comes closer to the spirit of what is meant by a chemical system--- several components to achieve an aggregate function. In this case, catalysts, structured arrays of microspheres, and the exploitation of a spherical p-n junction allow a novel way to effectively put two p-n Si solar cells in series with an electrolyte solution to split HBr with light. However, molecular chemists likely see few avenues for creative contribution in the "synthesis" of such systems.

Semiconductor-based devices for unidirectional electron transfer do, however, afford considerable opportunity for molecular scientists, and inorganic chemists especially. For example, it is now known that catalysis of  $\text{H}_2$  evolution from p-type semiconductor photoelectrodes is generally required in order to achieve high efficiency for light-driven reduction of  $\text{H}_2\text{O}$ .<sup>23</sup> The best known catalysts are noble metals,<sup>24</sup> high work function materials that would typically be expected to form an ohmic contact to p-type semiconductors.<sup>20</sup> The formation of an ohmic contact is undesirable, because the photovoltage would be diminished significantly. Assemblies like that by represented Scheme V involve the use of molecule-based redox polymer such as that derived from hydrolysis of I or III that provides for a uniform, non-ohmic contact to the p-type semiconductor.<sup>25</sup> The





Scheme IV. Texas Instruments system<sup>22</sup> for converting sunlight to stored chemical energy via the light-driven decomposition of  $2\text{HBr}$  to  $\text{H}_2$  and  $\text{Br}_2$ . Microspheres ( $\sim 100\mu\text{m}$ ) of crystalline Si are initially doped to have either a p-core and an n-skin or n-core and p-skin. The microspheres are dispersed into a "monograin" film (in a glass support), etched so that the core can be ohmically contacted, and coated with catalysts for  $\text{H}_2$  and  $\text{Br}_2$  generation. The result is a system for cleverly having two p-n Si solar cells in series and utilizing Si in an especially effective way.



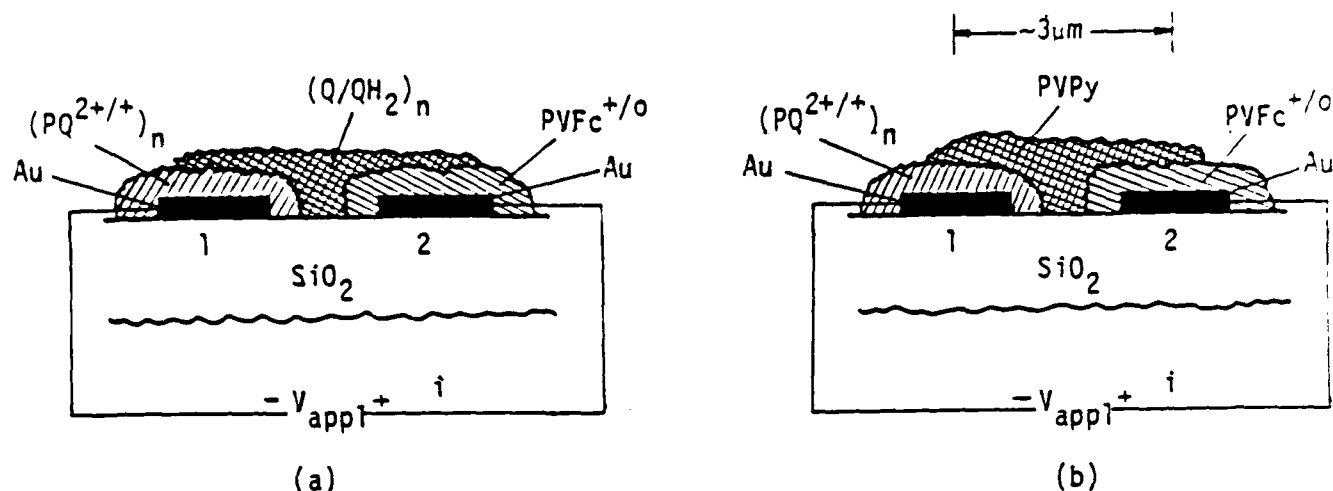
Scheme III. A double photoelectrode-based cell for converting light to chemical energy via the light-driven decomposition of  $H_2O$  to  $H_2$  and  $1/2O_2$ .<sup>21</sup> The net reaction requires eight photons per molecule of  $O_2$ , four at each photoelectrode, as in the natural photosynthetic system.

photoelectrode cell for water splitting.<sup>21</sup> However, such a system is not what would ordinarily be regarded as molecule-based, since the solid semiconductor is the light absorber, provides a mechanism for achieving charge separation, and its surface is the "catalyst" for converting one-redox-equivalent-at-a-time photogeneration events to multi-equivalent products such  $O_2$  from  $H_2O$  oxidation. Arguably, solid state photovoltaic cells can be used to duplicate the function of photosynthesis by placing the solar cell in series with an electrolyte solution. An especially clever device involves using microspheres of p-n Si, Scheme IV, to

by equation (8). Unlike the system where only one of the components is immobilized, there is no leakage current attributable to penetration of one molecule-based material into another. The small spacing between the microelectrodes allows significant steady state current to pass, despite the low "conductivity" of the redox polymers.

As developed above, the synthesis of a diode by interfacing two different molecule-based materials with closely-spaced microelectrodes has been effected by a rational strategy.<sup>39</sup> The asymmetrical current-voltage characteristic can be achieved. However, useful solid state diodes operate at high frequencies; the microelectrochemical diodes are not likely to be competitive in this respect. The time required to switch the microelectrochemical diode is that need to effect a change in redox state of a molecule-based material. Oxidation and reduction of electrode-confined polymers can be effected on timescales of the order of  $10^{-3}$  s for thicknesses of  $\sim 0.5 \mu\text{m}$  in the best cases. Diodes derived from molecule-based materials may have other properties that make them useful. Sensor applications are most easily envisioned in that the diode characteristics can be influenced by the chemical properties of the environment in a rational way.

As an example of a diode whose properties will depend on the chemical environment in a rational way consider the system represented by Scheme IX where the diode in Scheme VIII is elaborated in a way that places a third molecule-based material,  $(Q/QH_2)_n$ , between the  $(PQ^{2+}/^+)_n$  and  $PVFc^{+}/^0$  such that the only mechanism for charge transport from one microelectrode to the other is via the three molecule-based materials.<sup>40</sup> The key is that the formal potential of the  $(Q/QH_2)_n$  layer is pH-dependent, whereas the  $E^{\circ}$ 's of the other two molecule-based materials are pH-independent. Only when  $E^{\circ}(Q/QH_2)_n$  is between  $E^{\circ}(PQ^{2+}/^+)_n$  and  $E^{\circ}(PVFc^{+}/^0)$  will electrons pass from the  $(PQ^{2+}/^+)_n$ -coated microelectrode. The pH of the environment will control the  $E^{\circ}$  of the  $(Q/QH_2)_n$  layer and variations in pH should, therefore,



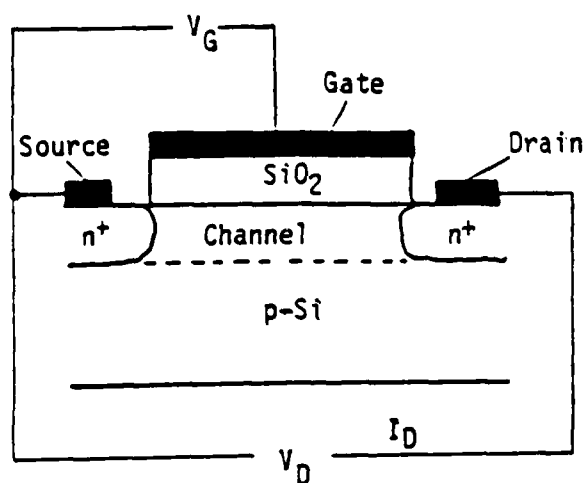
**Scheme IX.** (a) A microelectrochemical diode with a current that can be modulated by the solution pH, since the  $E^\circ$  of the  $(Q/QH_2)_n$  is pH sensitive and the  $E^\circ$ 's of the  $(PQ^{2+}/+)_n$  and  $PVFc^{+/0}$  polymers are independent of pH, and (b) a diode that responds to two chemical stimuli, pH and the presence of  $Fe(CN)_6^{3-/4-}$ .<sup>40</sup>

lead to variations in the current that can pass at an applied potential of  $\sim 0.9V$  when the negative lead is attached to the  $(PQ^{2+}/+)_n$ -coated microelectrode. Variations in this theme, Scheme IX, can lead to a diode where the steady-state current depends on the simultaneous presence of two chemical stimuli.<sup>40</sup> For example, consider replacing the  $(Q/QH_2)_n$  layer with polyvinylpyridine, PVPy. In an aqueous electrolyte the pyridine nitrogens can be protonated to form  $PVPyH^+$ .<sup>41,42</sup> However, the  $PVPy/PVPyH^+$  system does not have an  $E^\circ$  between  $E^\circ(PQ^{2+}/+)_n$  and  $E^\circ(PVFc^{+/0})$ . Thus, protonation alone does not turn on current. The  $PVPyH^+$ , though, can electrostatically bind very low concentrations of  $Fe(CN)_6^{3-/4-}$ ,<sup>41</sup> a redox couple with a formal potential between  $E^\circ(PQ^{2+}/+)_n$  and  $E^\circ(PVFc^{+/0})$ . What is achieved with the PVPy component is a system that passes current when both  $[H^+]$  and  $[Fe(CN)_6^{3-/4-}]$  are above certain values. Neither  $H^+$  nor  $Fe(CN)_6^{3-/4-}$  alone will allow current to pass.

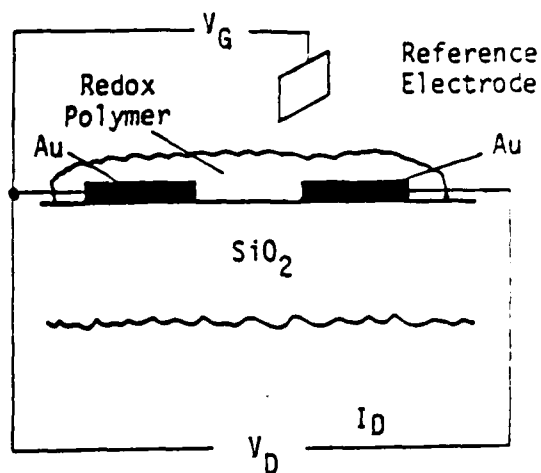
The ideas and systems developed in the foregoing discussion stem from research on the modifications of macroscopic electrodes.<sup>36</sup> Work by Murray,<sup>43</sup> especially, has established many of the basic concepts that can now be exploited, together with microfabrication, to synthesize new microelectronic devices. Indeed, Murray first demonstrated molecule-based diodes by functionalizing macroscopic electrodes with a "bilayer" of two different molecule-based polymers followed by deposition of a porous front contact to yield a "sandwich" structure with the crucial dimension being the thickness of the sandwich.<sup>43</sup> The systems represented in Schemes VIII and IX can be regarded as miniature, open-face sandwiches. There are many synthetic methodologies to be applied in devising molecule-based diodes and many challenges for molecular chemists. The utility of the diode systems will depend on the molecular properties of the components; durability, charge transport rates, and sensor specificity are areas.

Devices Inspired by Transistors. Narrowly defined, a transistor is a device that changes its resistance in response to an electrical signal.<sup>20</sup> This function is technologically very significant and existing applications for conventional transistors will be met by solid state devices. Nonetheless, a discrete Si/SiO<sub>2</sub>/metal field effect transistor, a so-called MOSFET (metal oxide semiconductor field effect transistor), bears many analogies to molecule-based transistors fabricated recently.<sup>44</sup> For molecule-based devices the nearest term application envisioned is to amplify chemical signals rather than to amplify electrical signals--- a typical function of solid state transistors.

To develop the analogy between molecule-based transistors and MOSFET devices<sup>20</sup> consider Scheme X. By changing the gate potential,  $V_G$ , of the MOSFET the region in the Si between source and drain and just beneath the SiO<sub>2</sub>, the "channel", can be changed from p-type Si (as in the bulk) to a region heavily n-type, or inverted in carrier density compared to the bulk; the Fermi level for electrons,  $E_F$ , can be



(a)



(b)

Scheme X. (a) A conventional Si MOSFET<sup>20</sup> and (b) a molecule-based transistor.<sup>44-4</sup>

moved from near the top of the valence band of the Si at the Si/SiO<sub>2</sub> interface to the bottom of the conduction band of the Si at the Si/SiO<sub>2</sub> interface. The consequence of carrier inversion in the channel is that at a fixed potential difference between source and drain,  $V_D$ , current flows between source and drain; the channel is said to be "open" and the device "on." When  $E_f$  is such that the channel region is p-type--- like the bulk,  $I_D = 0$  because the current path between source and drain is blocked by the nature of the  $n^+$ -p- $n^+$  junctions. For the purpose here the crucial point is that a variation of  $V_G$  of less than one volt results in a small amount of charge transfer, gate current,  $I_G$ , that dramatically changes the rate of charge transfer from source to drain at a given value of  $V_D$ . A MOSFET is typically turned off and on at  $>10^6$  Hz; the source-drain distance, channel length, is  $\sim 1\mu\text{m}$  in state-of-the-technology memory arrays; the  $\Delta V_G$  is  $\sim 0.5\text{V}$ ; and the



charge needed to open a closed channel can be as small as  $10^{12}$  charges/cm<sup>2</sup> of gate area.

A molecule-based microelectronic device that functions as a transistor can be synthesized by coating two closely-spaced microelectrodes, source and drain, with a polymer, the channel material, that has the property that a change in conductivity can be brought about by changing the electrochemical potential, Scheme X.<sup>44-47</sup> A polymer such as polyaniline has been demonstrated to be effective.<sup>46</sup>  $I_D$  has been shown to vary by  $\sim 10^7$  upon a change in  $V_G$  of 0.5V at  $V_D = 0.2V$ . While the similarities between the MOSFET and the molecule-based device are readily apparent there are three significant differences as well. First, the  $I_G$  in the molecule-based device is faradaic--- chemical oxidation and reduction occur to open and close the channel, whereas in the MOSFET the  $I_G$  is capacitive. The faradaic current necessarily involves movement of ions, a slower process than the movement of electrons in the solid state device. Accordingly, the molecule-based device will operate at much lower frequencies. Second, the molecule-based devices fabricated to date involve the use of a relatively large volume channel compared to the channel of a MOSFET, because the polymer is thick. Thus, though the source-drain separation is the same, the molecule-based device requires more charge to open and close the channel. Therefore, despite a similar  $\Delta V_G$  to open and close the channel the molecule-based device will consume more power, and this, coupled with the low mobility of ions, results in a molecule-based device that will only give power amplification at low frequencies. Improvements in the molecule-based devices will be made, but near term competition for solid state transistors in conventional applications is not realistic for any chemical or biological alternative.

The third difference between a solid state transistor and the molecule-based transistor may provide opportunities for practical applications: the channel of the

molecule-based device can respond directly to chemical signals; in general, the channel properties will depend on the medium in which it is immersed (solvent, electrolyte, etc.); and the  $V_G$  dependence of  $I_D$  at fixed  $V_D$  can be quite different for the molecule based device than for the MOSFET and depends on the channel material---a useful variable in the molecule-based device. Applications as sensors appear to follow from the properties of molecule-based transistors, especially when the device is elaborated with other molecular components to build in specificity to particular chemical signals.

Molecule-based transistor devices based on poly-3-methylthiophene illustrate one potential advantage of such a sensor.<sup>47</sup> The dependence of  $I_D$  and  $V_G$  reveals a characteristic that is at least as good as a state of the art MOSFET; a change in the redox potential,  $\Delta E_{\text{redox}}$ , of the solution in contact with the channel can cause a change in  $I_D$ ,  $\Delta I_D$ , that may be larger than can be obtained, from a similar  $\Delta V_G$  in solid state devices. However, whether a given redox reagent will equilibrate with the channel depends on the kinetics. Catalysts deposited onto, or dispersed throughout, the channel can endow the surface with a mechanism for equilibration with reagents that have slow kinetics such as  $O_2$  or  $H_2$ .<sup>46</sup> Attachments of enzymes directly onto the channel materials will allow specific reagents to be detected. Organized arrays of molecule-based transistors can be used to obtain a "fingerprint" response to a chemical environment. The point is that the remarkably strong dependence of  $I_D$  on  $V_G$  of certain molecule-based channel materials, coupled with the use of other molecular components, such as enzymes or synthetic redox catalysts, will allow the development of chemical detectors.

Another interesting fact is that the qualitative shape of the  $I_D$  vs.  $V_G$  curve can be qualitatively different for the molecule-based device compared to the MOSFET. A particular example is the polyaniline-based device<sup>46</sup> that shows a maximum in  $I_D$  at a particular value of  $V_G$  and  $\pm 0.2V$  around this value  $I_D$  falls by

severals orders of magnitude. This means that if a redox reagent is used to open the channel that only certain redox reagents will be thermodynamically well-matched to the purpose. By using a thin layer of a conventional redox polymer, e.g.,  $PVFc^{+}/0$ , on one microelectrode sandwiched between the channel material it may be possible to manipulate further the redox region where the device is turned on, since such an arrangement of two redox polymers can function as a diode as described in the preceding section. But when the  $PVFc^{+}/0$  is very thin the maximum magnitude of  $I_g$  will be largely controlled by the channel material spanning most of the region between the source and drain. The assertion is that molecule-based transistors, particularly ones based on two or more components, can be specific chemical detectors with a recognition step leading directly to amplification with the same system.

#### A Future for Synthesis of Chemical Systems

The four specific examples of "synthetic targets", multi-component catalysts, optical energy conversion systems, diodes and transistors, represent modest, but nonetheless complicated extensions of what is known. Doubtless there will be those who hold the view that such chemical synthesis is too applied to represent a pure research endeavor and that the preparation of so-called chemical systems is a mere, but expensive, summation of existing knowledge. However, taken to the extreme, such a view should lead to the demise of chemistry as an experimental science. After all, thermodynamics and quantum mechanics should be able to provide the predictive power needed for molecular or systems synthesis. It is the view of this author that systems synthesis is an important step in the development of new applications of molecular science, but there are a multitude of basic knowledge areas that will require major expansion prior to achieving significant practical impact. These include reactions at interfaces, physical characterization techniques, synthetic and purification methods for macromolecular assemblies, and theoretical understanding of

aggregate systems. Systems synthesis will require greater resource expenditure; there will be a new level of interdisciplinary effort required within and between groups; the research work will have longer gestation periods before the fruits will reach maturity; greater levels of patience are required from investigators and funding agencies; more planning for longer term projects will be required. The power of molecular synthesis is great--- it is time to add a new dimension to synthesis that is already, and will continue to be, rich in practical value. Catalysts, dyes, drugs, insecticides, and other single component, molecular materials will continue to be important, but there is much fundamental and, potentially, practical pay-off in the synthesis of multi-component, molecule-based systems. Rather than the traditional macroscopic to microscopic in electronics, there is a genuine opportunity for the fabrication of new systems from the "molecul up". Such devices may lead to new technological opportunities inspired by the existence of molecule-based biological systems for memory, pattern recognition, vision, and energy conversion.

#### Acknowledgements.

Work on energy conversion discussed in this article and cited in the references has been supported by the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences. The work on diodes and transistors was supported, in part, by the Office of Naval Research and the Defense Advanced Research Projects Agency. Numerous discussions with Professors H. Ehrenreich (Harvard), T.C. McGill (Caltech), D.K. Ferry (Arizona State) while at DARPA's Materials Research Council are also gratefully acknowledged.

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